Supplementary information

Ambient and Green Processing of Lead-free Double Perovskite Cs₂AgBiBr₆ Films

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Experimental section:

Materials: Quartz glass substrates, patterned ITO-glass substrates, and spiro-OMeTAD (99.0%) were purchased from Ossila. Cesium bromide (CsBr, 99.9%), Silver bromide (AgBr, 99.5%), bismuth (III) bromide (BiBr₃, 99%), Hellmanex III detergent were purchased from Thermo Fisher Scientific. Ethyl acetate (EA, 99.8%, anhydrous), dimethyl sulfoxide (DMSO, 99.8%, anhydrous), chlorobenzene (CB, 99.9%), 4-tert-butylpyridine (4-tBP, 98%), titanium diisopropoxide bis(acetylacetonate) (TTDP, 75 wt% in isopropanol), 1-butanol, acetonitrile (99.8%) and bis(trifluoromethane)sulfonimide lithium salt (LiTFSI, 99.95%) were purchased from Merck. 18NR-T titanium dioxide (TiO₂) paste was purchased from Greatcell Solar Materials. FTO-glass substrates were purchased from Pilkington.

Preparation of Cs₂AgBiBr₆ precursor solution: 213 mg CsBr, 94 mg AgBr, and 224 mg BiBr₃ were dissolved in 1 mL of DMSO and stirred vigorously at 70°C for 1 hour to form a homogeneous and clear solution. For ambient-processed Cs₂AgBiBr₆ films, the entire precursor solution preparation was conducted in ambient air with a relative humidity (RH) of 60–70%. In contrast, for glovebox-processed Cs₂AgBiBr₆ films, the solution preparation was performed in a glove box with a moisture level of ~1 ppm.

Deposition of Cs₂AgBiBr₆ film: Quartz glass, FTO-glass, or ITO-glass substrates were cleaned in an ultrasonic bath following the sequence of using 2% Hellmanex detergent in deionized water, ethanol, and deionized water, followed by UV–ozone treatment for 15 minutes. The substrates were preheated at 70°C on a hotplate before precursor deposition. For pristine film deposition, the preheated substrate was transferred to a spin coater, where 80 μ L of the Cs₂AgBiBr₆ precursor solution was spin-coated at 4000 rounds per minute (rpm) for 30 seconds. The resulting film was then annealed on a hotplate at 280°C for 5 minutes to complete film formation. For EA treatment, 200 μ L of EA was rapidly dripped onto the spinning substrate between the 7th to 8th second after the spin-coating process started. The remaining processing steps were identical to those used for the pristine Cs₂AgBiBr₆ films.

Fabrication of Ambient-Processed Solar Cells: After cleaning and exposing the patterned ITO-glass substrates to UV–ozone treatment for 15 minutes, a compact TiO₂ layer was deposited by spin-coating 0.1 M TTDP dissolved in 1-butanol at 2000 rpm for 40 seconds, followed by drying at 100°C for 10 minutes in ambient air. A second layer of TiO₂ was deposited by spin-coating 0.3 M TTDP in 1-butanol and dried following the same steps as the first layer. Next, a mesoporous TiO₂ layer was formed by spin-coating a diluted 18NR-T TiO₂ paste (1:5 weight ratio in ethanol) at 4500 rpm for 30 seconds, followed by annealing in a furnace at 450°C for 15 mins. The mesoporous TiO₂ coated substrates were then preheated at 75°C for 15 mins. The Cs₂AgBiBr₆ precursor solution filtered through a 0.45 μ m PES syringe filter was subsequently deposited onto the preheated substrates following the procedure described earlier for pristine and EA-treated films. To fabricate the hole transport layer, 80 μ L of spiro-OMeTAD solution was spin-coated at 4000 rpm for 30 seconds. The

spiro-OMeTAD solution was prepared by dissolving 43 mg of spiro-OMeTAD in 0.5 mL of CB, followed by the addition of 10 μ L of Li-TFSI solution (520 mg Li-TFSI in 1 mL acetonitrile) and 15 μ L of 4-tBP. Finally, ~90 nm of Au was deposited via thermal evaporation to complete the device fabrication. Except for the thermal evaporation step, all solution preparation and fabrication processes were performed in ambient air under an RH of 50–70%.

Characterizations: Zeiss Ultra 55 FEG-SEM and JEOL 7001F FEG-SEM were used to examine the surface morphology and cross-section of the films, as well as to perform EDX analysis. XRD patterns were obtained using a Rigaku SmartLab diffractometer with Cu K α radiation (λ = 1.5406 Å) at a scan rate of 0.01°/min. The Xray tube voltage and current were set to 40 kV and 30 mA, respectively. State-state PL spectra were recorded using an Edinburgh Instruments FLS980 spectrophotometer. UV-vis-NIR absorption spectra were measured with a Shimadzu UV-2401PC spectrophotometer. XPS spectra were acquired using a Scienta Omicron highthroughput XPS system with a monochromatic AI K α source (*hv* = 1486.7 eV). Survey spectra were recorded with a pass energy of 150 eV and an energy step of 0.5 eV, while high-resolution core-level spectra were obtained with a pass energy of 50 eV and an energy step size of 0.1 eV. A neutralizer was applied to mitigate surface charging effects. Data analysis and quantification were performed using CasaXPS software, with background subtraction using the Briggs and Grant Tougaard model and peak fitting using a GL(30) lineshape.¹ All spectra were calibrated to the adventitious hydrocarbon (sp³ C) peak at 284.8 eV. Current density-voltage (J-V)measurements were performed using an Ossila push-fit test board and a Keithley 2400 source meter under both dark conditions and simulated AM1.5 sunlight (100 mW cm⁻ ²) from an Oriel class AAA solar simulator. The light intensity was calibrated using a Newport-certified quartz-filtered Si reference cell. The J-V curve scan rates were set at 200 mV/s or 400 mV/s.



Fig. S1 Photographic image of precursor solution of Cs₂AgBiBr₆ prepared by dissolving CsBr, BiBr₃, and AgBr salts in a molar ratio of 2:1:1 in the DMSO



Fig. S2 Photographic images of actual pristine and EA-treated Cs₂AgBiBr₆ films coated on the ITO-glass fabricated in the ambient air.



Fig. S3 Top surface SEM and EDX elemental mapping of Bi, Ag and Cs elemental distribution for the ambient-processed pristine and EA-treated Cs2AgBiBr₆ film.



Fig. S4 Atomic concentrations of Cs, Ag, Bi, Br, Si, and O quantified by XPS for the ambient-processed pristine and EA-treated Cs2AgBiBr₆ film.



Fig. S5 High-resolution core-level XPS spectra of the Br 3d for the ambient-processed pristine and EA-treated Cs2AgBiBr₆ film.



Fig. S6 Tauc plot of the indirect bandgap ambient-pristine Cs₂AgBiBr₆ films.



Fig. S7 V_{OC} and FF distribution for the PSCs based on the ambient-processed pristine and EA-treated films.



Fig. S8 *J*–*V* curves under AM1.5 sunlight under various scan rates and cycles for the PSCs based on the ambient-processed pristine and EA-treated films. The first and second scan rates were set at 200 mV/s and the fast scan rate were set at 400 mV/s.



Fig. S9 Forward and reverse scan J-V curves for the PSCs based on the ambientprocessed pristine and EA-treated films.

Table S1. FWHM values extracted from the XRD patters for ambient-processed pristine and EA-treated Cs₂AgBiBr₆ films.

| Deflections | FWHM | FWHM | | |
|-------------|------------|--------------|--|--|
| Renections | (Pristine) | (EA-treated) | | |
| 200 | 0.15° | 0.16° | | |
| 220 | 0.16° | 0.20 ° | | |
| 400 | 0.19° | 0.18° | | |

Table S2. Binding energy of doublets of Cs 3d, Ag 3d, Bi 4f, and Br 3d for ambientprocessed pristine and EA-treated Cs₂AgBiBr₆ films (Fitting error \pm 0.1 eV).

| | Cs | Cs | Ag | Ag | Bi | Bi | Br | Br |
|------------|-------------------|-------------------|-------------------|-------------------|--------------------------|--------------------------|-------------------|-------------------|
| Sample | 3d _{3/2} | 3d _{5/2} | 3d _{3/2} | 3d _{5/2} | 4f _{5/2} | 4f _{7/2} | 3d _{3/2} | 3d _{5/2} |
| Drictino | 738.28 | 724.33 | 373.71 | 367.71 | 164.00 | 158.70 | 68.88 | 67.85 |
| Filsune | eV | eV | eV | eV | eV | eV | eV | eV |
| EA treated | 738.47 | 724.50 | 373.68 | 367.73 | 164.06 | 158.66 | 68.93 | 67.88 |
| | eV | eV | eV | eV | eV | eV | eV | eV |

Table S3. A summary of photovoltaic parameters for the multiple PSCs based on the ambient-processed pristine and EA-treated films.

| Sample | PCE (%) | FF (%) | J _{SC} (mA/cm²) | V _{oc} (mV) | |
|------------|-------------|--------------|--------------------------|----------------------|--|
| Pristine | 0.11 ± 0.05 | 56.32 ± 9.05 | 0.30 ± 0.15 | 640.97 ± 101.12 | |
| (Champion) | 0.21 | 48.11 | 0.58 | 742.70 | |
| EA-treated | 0.71 ± 0.18 | 61.61 ± 3.81 | 1.12 ± 0.21 | 1027.12 ± 28.29 | |
| (Champion) | 1.08 | 68.86 | 1.57 | 999.16 | |

Table S4. Categorization of solvents and antisolvents used to fabricate $Cs_2AgBiBr_6$ based on their Safety (S), Health (H), and Environment (E) scores obtained from the CHEM21 solvent guide and their associated physical properties such as flash point (FP), boiling point (BP), and associated worst health hazardous H3xx statements.^{2,3} A high score indicates a higher level of hazardous score: green: 1–3 (recommended), yellow 4–6 (problematic), and red 7–10 (hazardous).

| Solvents | Worst | FP | BP | S | н | Е | overall | |
|--------------|-------|------|------|-------|-------|-------|-------------|--|
| | H3xx | (°C) | (°C) | score | score | score | | |
| DMF | H360 | 58 | 158 | 3 | 9 | 5 | Hazardous | |
| DMSO | None | 95 | 185 | 1 | 1 | 5 | Problematic | |
| Antisolvents | | | | | | | | |
| СВ | H332 | 29 | 132 | 3 | 2 | 7 | Problematic | |
| IPA | H319 | 12 | 82 | 4 | 3 | 3 | Recommended | |
| MA | H302 | -10 | 57 | 5 | 3 | 5 | Problematic | |
| EA | H302 | -4 | 77 | 5 | 3 | 3 | Recommended | |

Health hazardous statements: H302: harmful if swallowed, H319: causes serious eye irritation, H332: harmful if inhaled, H360: may damage fertility or unborn child.

Reference:

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- D. Prat, A. Wells, J. Hayler, H. Sneddon, C. R. McElroy, S. Abou-Shehada and P. J. Dunn, *Green Chem.*, 2016, **18**, 288–296.
- 3 F. Meng, L. Cheng, F. Wang, K. Chen, Z. Sun and G. Wang, *Adv. Sustain. Syst.*, 2025, **9**, 2400695.